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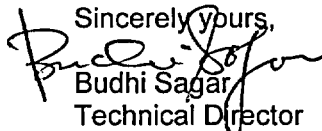
Subject: Programmatic Review of Abstract

Dear Mrs. DeMarco:

The enclosed abstract and NRC Form 390A are being submitted for programmatic review. This extended abstract is planned to be made available to conference attendees at the International Workshop on Colloids and Colloid-Facilitated Transport of Contaminants in Soils and Sediments, to be held September 19–20, 2002, in Tjele, Denmark. The title of the abstract is

> Transport of Plutonium by Inorganic Colloids: From Laboratory Tests to Field-Scales Applications by V. Cvetkovic, S. Painter, D. Pickett, and D. Turner

The paper will be presented by Dr. V. Cvetkovic who is a CNWRA consultant who resides in Sweden. This abstract is a product of the CNWRA and do not necessarily reflect the view(s) or regulatory position of the NRC.

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Transport of Plutonium by inorganic colloids: From laboratory tests to field-scale applications

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Summary

We investigate the potential impact of inorganic colloids on plutonium transport in the alluvial aquifer near Yucca Mountain, Nevada. Our emphasis is on sorption kinetics: If sorption on colloids is reversible and relatively rapid, then the effect of colloids on nuclide transport is negligible in most cases. We first evaluate the laboratory data on sorption of plutonium by colloids [4,5], and estimate the "slow" forward sorption rate [7]. Transport computations are made for the alluvial aquifer near Yucca Mountain, using a configuration analogous to the one in [6]. A flow path (streamtube) connects a hypothetical injection of Pu into the alluvial aquifer, with a compliance boundary 8 km [8752 yd] downstream [6]. We compute the probability of the steady-state, total Pu discharge (i.e., dissolved and colloid-bounded) across the compliance boundary as a function of system parameters. Sorption is assumed to be bi-linear or linear, reversible or irreversible, and Pu is injected into the aquifer at a constant rate J_0. Without colloids, the median Pu discharge is essentially zero ($10^{-24} J_0$). In comparison, the corresponding median Pu discharge with colloids is in the range $(0.08 - 0.7) J_0$.

Introduction

If sorption on colloids is reversible and relatively rapid, then the effect of colloid facilitated nuclide transport (CFNT) is for most practical purposes negligible, given the relatively low colloidal concentrations found in aquifers. Only if binding of tracers on colloids is irreversible (or slowly reversible) relative to the time scale of the transport problem, may colloids play a potentially significant role in subsurface contaminant transport. Thus, understanding and characterizing the kinetics of sorption on colloids is a critical step in obtaining accurate assessments of CFNT in groundwater.

In this study we first estimate the "slow" kinetic sorption rate [7] based on laboratory tests [4,5] for Pu on four colloid types. Next, we summarize results of a sensitivity analyses both in terms of sorption models (bi-linear or linear, reversible or irreversible) and model parameters. We use sorption rates as estimated from data [4,5] to assess the possible impact of CFNT specifically for Pu in the alluvial aquifer near Yucca Mountain.

Materials and methods

A series of laboratory tests were carried out at the Los Alamos National Laboratory by Lu and co-workers with the purpose of studying sorption on colloids [4,5]. Colloids of different minerals were considered (Hematite, Smectite, Montmorillonite, Silica), with four different actinides (Plutonium, Americium, Neptunium and Uranium), in two types of waters samples (natural and synthetic), with varying colloidal concentration (from 0.05 to 1 g/L [$0.29 \cdot 10^{-4}$ to $5.78 \cdot 10^{-4}$ oz/cu in]), temperature (20, 40, and 80°C [68, 104 and 176°F]), and ionic strength (from 0.005 M to 0.134 M [$8.2 \cdot 10^{-5}$ to $2.2 \cdot 10^{-3}$ mol/cu in]). The kinetics of sorption in the

experiments reported in [4,5] was recorded up to 10 days. We shall focus here on sorption of Plutonium in natural groundwater samples which is provided for reference case conditions: particle size in the range 70-100 nm [2.7-3.9 · 10^{-6} in], ionic strength of 0.005 M [8.2 · 10^{-5} mol/cu in], temperature of 20^0 C [68^0F] and pH of 8.2. The adsorbed Plutonium fraction was measured at following times: 1h, 4h, 24h, 48h, 96h and 240h.

For evaluating the laboratory sorption data of Lu et al. [4,5], we derived an analytical solution for a two-site sorption model [7]. If the reverse rate of the "slow" sites is small relative to the experimental time, the solution at the irreversible limit is obtained as

$$C(t)/C_0 = \frac{1}{2} e^{(B-A/2)t} + \frac{1}{2} e^{-(B+A/2)t} + \frac{1}{2B} \left(k_r - \frac{A}{2} \right) \left[e^{(B-A/2)t} - e^{-(B+A/2)t} \right] \quad (1)$$

$$A \equiv k_f + k_r + \alpha_f \quad ; \quad B^2 \equiv \frac{A^2}{4} - k_r \alpha_f$$

where C/C_0 is the normalized Pu concentration in the solution, k_f [1/T] is the forward "fast" rate, k_r [1/T] is the reverse "fast" rate, and α_f [1/T] is the forward "slow" rate, in this case equivalent to the irreversible transfer rate. The adsorbed fraction is computed as $1 - C/C_0$.

Our basic configuration for the alluvial aquifer at Yucca Mountain is analogous to the one presented in [6]. Once the engineered barriers have been breached, the radionuclides must travel through three natural subsystems before reaching the compliance boundary specified in Title 10 of the U.S. Code of Federal Regulations, Part 63. Since the focus here is on process-level sensitivities, we consider a continuous release with a constant rate of Pu at the upstream side of the alluvial aquifer and calculate the discharge at the compliance boundary. This allows us to isolate the alluvium barrier from the other components in the repository system and probe its efficacy as a transport barrier with respect to colloid facilitated nuclide transport.

The basic assumptions/conditions for our present analysis are summarized as follows:

- *Flow/advection:* (i) Hydraulic conductivity in the aquifer is heterogeneous; (ii) dominant hydrodynamic mode of transport is advection, whereby local (pore-scale) dispersion is neglected; (iii) groundwater flow is at steady-state.

- *Nuclide:* (i) Pu mass is injected into the aquifer at a constant rate, $J_0 = 10^{-4}$ g/yr [3.5 · 10^{-6} oz/yr], over a hypothesized area $A_0 = 0.01$ m^2 [15.5 sq in] with a volumetric flow rate q [L^3/T]; the boundary condition for transport is thus assumed as $J_0 H(t)$, where $H(t)$ is the Heaviside step function; (ii) Pu sorbs onto the solid (immobile) phase at equilibrium; (iii) sorption of Pu on colloids can be described with a bi-linear sorption model with S_m [M/L^3] as the maximum sorbed concentration for a given colloidal concentration C_c [M/L^3].

- *Colloids:* Natural inorganic colloids move with groundwater velocity, i.e., retention and/or removal/generation of colloids is neglected; hence, colloidal concentration C_c [g/L] is uniform and at steady-state.

For transport calculations, we consider steady-state mass balance equations for Pu concentration in solution (C [M/L^3]) and on colloids (S [M/L^3]). Under above assumptions, these are given by

$$\frac{dX}{d\tau} = -\alpha X \left(Y_m - Y \right) + \alpha_r Y - \lambda R X \quad ; \quad \frac{dY}{d\tau} = \alpha X \left(Y_m - Y \right) - \alpha_r Y - \lambda Y \quad (2)$$

where $Y_m \equiv S_m q/J_0$, $X \equiv Cq/J_0$ and $Y \equiv Sq/J_0$ are dimensionless, $\alpha = \alpha_f/Y_m$ [1/T], α_r [1/T] is the reverse rate, R is the retardation factor for Pu in the alluvial aquifer, λ [1/T] is the decay rate, and τ is the groundwater residence time. The normalized total nuclide discharge is defined as $Z = X + Y$. Note that eq.(2) is a Lagrangian formulation of transport since the independent variable is the groundwater residence time τ, which is given statistically [1,2]. In the following, we shall compute the probability of Z as a function of system parameters.
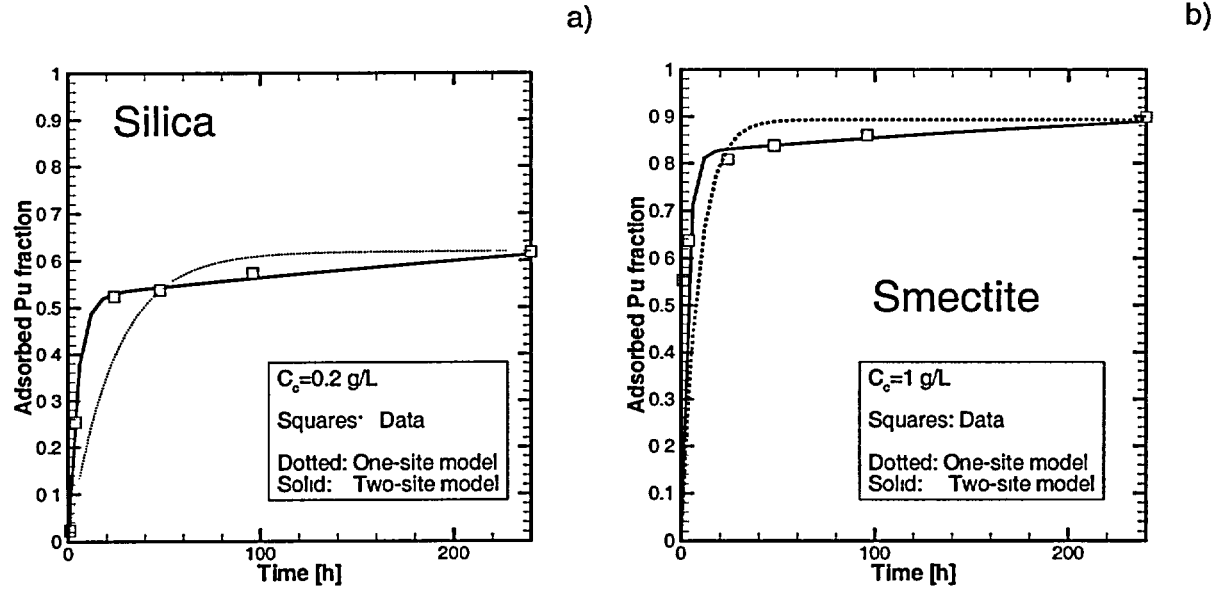
Results and discussion

Figure 1: One- and two-site sorption model calibration using laboratory data from Lu et al. [4,5] for: (a) Silica with $C_c = 0.2$ g/L, and (b) Smectite with $C_c = 1$ g/L. Note: 1 g/L=5.78·10^{-4} oz/cu in.

The best fit curves are exemplified in Fig. 1 for two minerals, Silica and Smectite. The data set for Silica exhibits a clear linear increase of the adsorbed fraction in the range $24 \leq t \leq 240$ h (Fig. 1a). The two-site model provides a close match with the data. The one-site model in this case deviates for all but two data points (1 h and 48 h, Fig. 1a). The data points for Smectite exhibit a rapid and relatively large increase of adsorbed Pu fraction over a short time (up to 24 h) and then a relatively small, linear increase of $1 - C/C_0$ between 24 h and 240 h. The two-site model provides a close match with all data points except the first (at 1 h). By contrast, the one-site data model provides a poor match with all but two data points (24 h and 240 h, Fig. 1b). The calibrated range of the forward sorption rate α_f for all considered minerals is 0.0017-0.02 1/h. If we assume that α_f is proportional to C_c [8], then we can define an intrinsic rate as $\alpha_0 \equiv \alpha/C_c$ [1]. The range of α_0 was found as 0.0017-0.1 L/(g h) [2.9-173 cu in/(oz yr)].

Our basic concept for transport is a single flow path (streamtube) which extends through the alluvial aquifer, from the tuff to the compliance boundary [6]. The volumetric flow rate q for a single flow path is assumed perfectly correlated to the groundwater residence time τ and computed as $q = A_0 L n/\tau$, where n is the aquifer porosity and L the transport distance. We assume $n = 0.25$, $L = 8$ km [8752 yd], a log-normal distribution with mean and variance of 4×10^3 yr and 12.4×10^6 yr^2 for τ, consistent with previous work [6]. We use values

$R = 1800$ and $\lambda = 10^{-5}$ 1/yr for Pu. The system (2) is solved numerically using the Runge-Kutta method.

Colloidal concentration data is available from three wells in the the Pahute Mesa area [3] and is in the range $C_c = 0.48 - 0.73$ mg/L [2.72-4.22·10^{-7} oz/cu in]; we consider $C_c = 0.6$ mg/L [3.47·10^{-7} oz/cu in] to be representative for the alluvial aquifer. Two approaches are implemented to estimate the maximum concentration S_m. The two approaches yield considerably different values for S_m (in the range $10^{-7} - 10^{-4}$ g/L [5.78-5780·10^{-11} oz/cu in] [2]), which we shall use for sensitivity analysis. The "irreversible" sorption rate α_f is estimated in [7] as summarized above. We consider 0.007 1/h (or 33 1/yr) as a representative value for α_f, and determine a representative intrinsic sorption rate as $\alpha_0 = 165$ L/(yr g) [2.85·10^5 cu in/(oz yr)]. With $C_c = 0.6$ mg/L [3.47·10^{-7} oz/cu in], we estimate the forward sorption rate for the alluvial aquifer as $\alpha_f = 0.1$ 1/yr, and consider this a fixed value. Since transport times are much larger than the time scale of laboratory tests, the sorption on colloids may be reversible to some extent. The degree of "reversibility" is quantified by a ratio $a \equiv \alpha_f/\alpha_r$; $a = \infty$ indicates the irreversible case ($\alpha_r = 0$). We have currently no site-specific data on α_f [1/T] (or a) and shall use it here as a sensitivity parameter.

The complementary cumulative distribution function (CCDF) of the total Pu normalized discharge, Z, is illustrated in Fig. 2 for different "reversibility" ratios a, and for limiting values of S_m. In Table 1 we summarize the median value $Z_{50\%}$ as a function of S_m and the ratio a. We find that increasing a suppresses the effect of variability in τ such that the CCDFs converge to a step function form. The effect of heterogeneity and τ variability is most pronounced for the strongly reversible case (i.e., for relatively low a, Fig. 2). This implies that if CFNT is the dominant transport mechanism for safety assessment, then the characterization of the hydraulic heterogeneity may be less important, compared to the characterization of the colloid-nuclide exchange properties.

For large S_m, the linear model provides a reasonable approximation of the bi-linear model provided that "reversibility" is low, $a > 1000$. For small S_m, the linear model overestimates the bi-linear model for $a > 100$, and underestimates for $a < 10$ (strong reversibility) (Table 1). In the case of decreasing $a < 10$ (strong reversibility), both models yield rapidly decreasing $Z_{50\%}$, however, the linear model predicts a faster decrease than the bi-linear model. If we consider the range $S_m = 10^{-6} - 10^{-5}$ g/L [57.8-578·10^{-11} oz/cu in] with $a > 1000$ (i.e., relatively low reversibility) as most realistic for the alluvial aquifer, then $Z_{50\%}$ is found in the interval 0.08-0.7 (where the linear model predicts 0.63 for $a > 100$, Table 1). In the high probability range, we find $Z_{95\%} = 0.02 - 0.2$, where the linear model provides a conservative estimate as 0.31 (Table 2).

Table 1: Summary of the median normalized total Pu discharge Z (denoted by $Z_{50\%}$) for different reversibility ratios $a = \alpha_f/\alpha_r$ and maximum concentration S_m, for fixed $\alpha_f = 0.1$ 1/yr. Note: 1 g/L=5.78·10^{-4} oz/cu in.

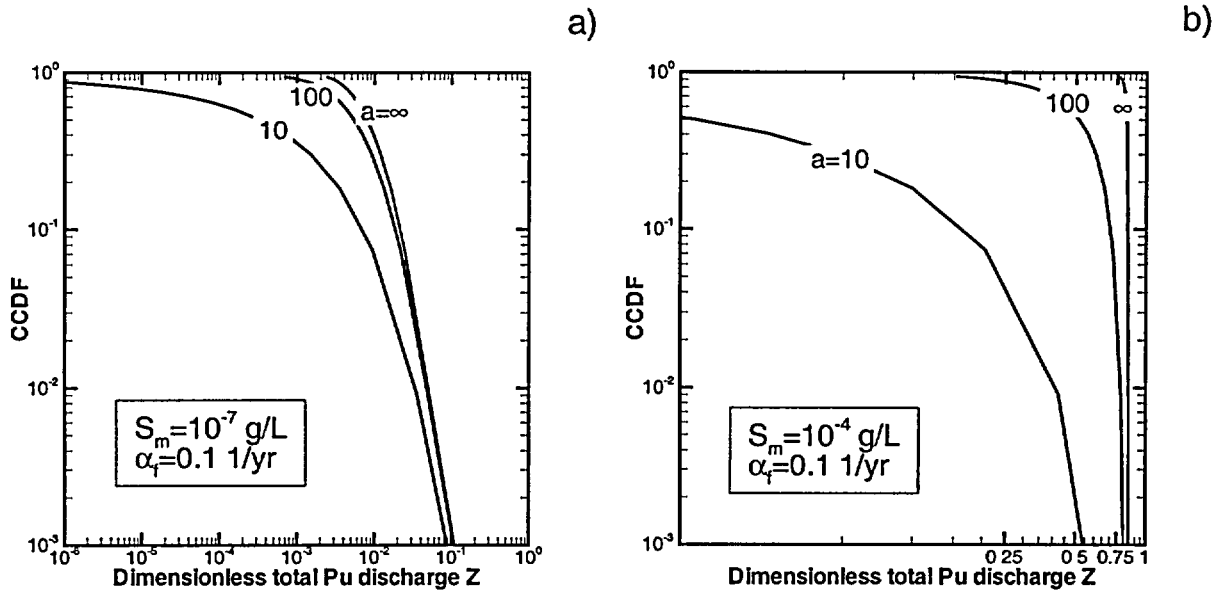| $Z_{50\%}$	$S_m = 10^{-7}$ [g Pu/L]	$S_m = 10^{-6}$ [g Pu/L]	$S_m = 10^{-5}$ [g Pu/L]	$S_m = 10^{-4}$ [g Pu/L]	Linear Model
$a = \infty$	0.00796	0.07963	0.82204	0.82237	0.82241
$a = 1000$	0.00762	0.07621	0.72040	0.78386	0.63126
$a = 100$	0.00539	0.05390	0.40144	0.51396	0.04467
$a = 10$	0.00033	0.00308	0.00971	0.01158	0

a) b)

Figure 2: Complementary cumulative distribution functions (CCDFs) of the normalized total Pu discharge $Z = X + Y$ at the compliance boundary, with: (a) $S_m = 10^{-7}$ g/L, and (b) $S_m = 10^{-4}$ g/L. Note: 1 g/L=$5.78 \cdot 10^{-4}$ oz/cu in.

Table 2: Same as Table 1; $Z_{95\%}$ is the value of Z with 95% probability of occurrence. Note: 1 g/L = $5.78 \cdot 10^{-4}$ oz/cu in.

$Z_{95\%}$	$S_m = 10^{-7}$ [g Pu/L]	$S_m = 10^{-6}$ [g Pu/L]	$S_m = 10^{-5}$ [g Pu/L]	$S_m = 10^{-4}$ [g Pu/L]	Linear Model
$a = \infty$	0.00237	0.02368	0.24798	0.76677	0.76681
$a = 1000$	0.00203	0.02031	0.20308	0.64016	0.31348
$a = 100$	0.00068	0.00678	0.06365	0.15285	0.00004
$a = 10$	0	0	0	0	0

Conclusions

We evaluated the laboratory data from Lu et al. [4,5] using a two-site batch sorption model in order to estimate the (slow) sorption rate α_f. Five kinetic sorption data sets for plutonium on four types of colloids (Hematite, Montmorillonite, Silica and Smectite) in natural groundwater samples were considered. The rate α_f was estimated in a one-order of magnitude range, 0.02-0.0017 1/h.

For the estimated conditions in the alluvial aquifer near Yucca Mountain, we found that the impact of colloids may be significant for plutonium, relative to the situation without colloids. With J_0 being the Pu injection rate, we found that the median of the Pu discharge from a single canister across the compliance boundary is in the range $(0.08 - 0.7)J_0$. The predicted interval with high confidence (95% probability) is $(0.02 - 0.2)J_0$. In other words, the conservative, high probability estimate is 20% of J_0. This can be compared to the case without colloids, where the median Pu discharge $(Z_{50\%})$ is essentially zero $(10^{-24}J_0)$. We emphasize that this analysis is intended to address the potential effect that colloids may have on one barrier in a multiple barrier system. To what extend colloid facilitated transport affects

the full-system performance depends on several other considerations such as the waste package failure scenario, the effects of engineered barriers, retardation in the unsaturated zone, dilution at the compliance boundary and physical filtration of colloids, issues that are outside the scope of this work.

Acknowledgments

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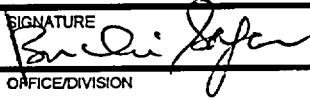6220 Culebra Road
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